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Studies of structural and electrical properties of some tungsten-bronze ferroelectric ceramics

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Abstract : Polycrystalline samples of $Ba_5RTi_2ZrNb_7O_{30}$ [R–Sm, Gd] of Tungsten Bronze (TB) structural family have been prepared by a high temperature solid-state reaction technique, X-ray diffraction (XRD) analysis as a function of temperature shows the orthorhombic structure of the compounds at room temperature. Dielectric studies at four different frequencies, 1,10, 100 kHz and 1 MHz, show that the above compounds have ferroelectric phase transition of diffuse type, and also have relaxor properties

Keywords : Ferroelectric, tungsten-bronze, diffuse phase transition, orthorhombic.

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1. Introduction

Since the discovery of ferroelectricity in $BaTiO_3$ [1], a large number of inorganic oxides of different structural families (*i.e.* Pervoskite, Tungsten-Bronze, Pyrochlore, Spinel *etc.*) and chemical formula have been studied in the past in search of new materials for industrial applications [2,3]. One of the crystal families of oxygen octahedral ferroelectric is the tungsten-bronze (TB) structure, which has a general formula $(A_1)_2(A_2)_4(C)_4(B_1)_2(B_2)_8O_{30}$. A wide variety of cation substitution is possible here because of the presence of many interstices like A_1, A_2, B_1, B_2, and C [4]. This substitution can improve some physical properties like transducers, computer memory and display, electro-optic, elasto-optic and pyroelectric found in some compounds of this family. After the discovery of barium sodium niobate (BNN) [5] as a good electro-optic material, a large number of niobate compounds of this family have been studied. For example, $Ba_2Na_3RNb_{10}O_{30}$ [6], $K_2LaNb_5O_{15}$ [7] $Ba_4NaNb_{10}O_{30}$ [8] compounds have been reported to have diffuse phase transition with different value of transition temperature. As there is no report on the proposed compounds which belong to TB structural family, we have systematically studied the structural and electrical properties of the proposed compounds of a general formula $Ba_5RTi_2ZrNb_7O_{30}$ [R = Sm,Gd] and reported the results here.

2. Experimental

Polycrystalline samples of $Ba_5SmTi_2ZrNb_7O_{30}$ and $Ba_5GdTi_2ZrNb_7O_{30}$ (referred to as A and B respectively) were prepared by high-temperature solid-state reaction technique. High purity raw materials used were : $BaCO_3$ (M/s BDH Chemical Ltd.), TiO_2 and Nb_2O_5 (99.9% M/s fine Chem. Ltd.) : ZrO_2 (99% Aldrich Chemical, USA), Gd_2O_3 (99% Indian Rate Earth Ltd., India). The stoichiometry mixtures of the weighed ingredients were thoroughly mixed in methanol in an agate mortar for 2 h and dried by slow evaporation. The air dried powder of the compounds were calcined at 1000°C for 24 h in a platinum crucible. The process of mixing and calcination was repeated until homogenous fine powder was obtained. Finally, cylindrical pellets of 1 cm diameter and 0.1–0.2 cm, thickness were compacted using a hydraulic press at a pressure of $6 \times 10^7 N/m^2$ using polyvinyl alcohol as a binder. The pellets were then sintered at 1200°C for 12 h. The formation of single phase compounds were checked by X-ray diffraction (XRD) technique using a diffractometer (Miniflex, Rigaku, Japan) with CuK_α radiation (λ = 1.5418A) in a wide range of Bragg angles 2θ ($20° \leq 2 \leq 70°$). The linear

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particle size of the compounds was calculated using Scherrer's equation $P=K\lambda/\beta_{1/2}\cos\theta$ where K = 0.89, $\beta_{1/2}$ = half peak width. To study the electrical properties, the pellets were electroded with high-quality silver paste. Measurements of dielectric constant (ε) and loss (tan δ) of the unpoled samples were obtained using a GR 1620-AP capacitance measuring assembly with a three-terminal sample-holder as a function of frequency (200 Hz to 1 MHz) at room temperature and temperature (liquid nitrogen to 400°C) at 1,10,100 kHz and 1 MHz frequencies.

The dc resistivity of all the samples was measured as a function of electric field (100 V/cm) and temperature (room temperature to 300°C) using a keithley 617 programmable electrometer. Temperature measurement with an accuracy of ±2°C was made with a chromel-alumel thermocouple.

3. Results and discussion

The room temperature XRD pattern of the calcined powders and sintered pellets of both the A and B compounds were found to be sharp with single diffraction peaks, indicating better homogeneity and crystallization of the samples. All the reflection peaks were indexed and the lattice parameters were determined in different crystal systems and cell configuration using a standard computer program 'PowdMult' with observed d-values of strong, medium and low intensity peaks spred over wide 2θ range. Finally, an orthorhombic unit cell was selected for which $\Sigma\Delta d = (d_{obs}-d_{cal})$ was found to be minimum. The good agreement between observed and calculated d-values (Table 1) supports the correctness of selected crystal system and unit cell parameters. The refined cell parameters obtained as above (in Å) for compound A are : a = 16.80, b = 13.61, c = 7.23 Å and for compound B are a = 13.21, b = 10.76, c = 9.99 Å. Using the XRD data the particle size was determined to be 239 Å for compound A and 262 Å for compound B.

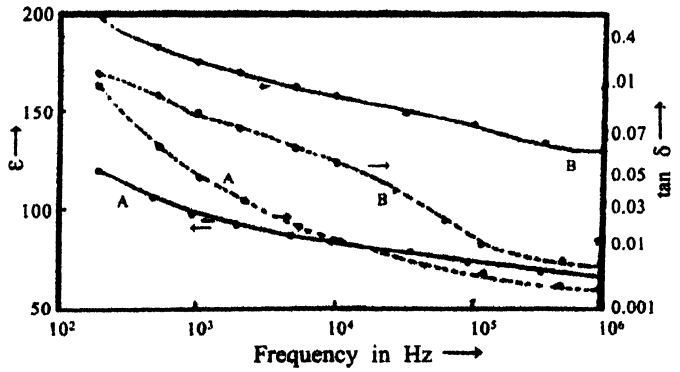

Figure 1. Variation of dielectric constant (ε) and loss (tanδ) of A and B compounds at room temperature.

Figure 1 shows the frequency (2×10^2 to 10^6 Hz) dependence of dielectric parameters (*i.e.* ε and tan δ) at room temperature of both the compounds. It have been observed that the value of the dielectric constant (ε) and tangent loss (tan δ) of the above compounds with increasing frequency indicates the normal behaviour of dielectrics/ferroelectrics [9].

Table 1. Comparison of observed (O) and calculated (C) d-values of some reflections of $Ba_5SmTi_2ZrNb_7O_{30}$ and $Ba_5GdTi_2Nb_7O_{30}$ ceramics at 300 K with relative intensity in parenthesis.

$Ba_5SmTi_2ZrNb_7O_{30}$		$Ba_5GdTi_2Nb_7O_{30}$	
h k l	*d* (Å)	*h k l*	*d* (Å)
1 1 1	(O) 3.4538 (24)	1 1 0	(O) 3.4678 (24)
	(C) 3.4538		(C) 3.4678
1 0 2	(O) 3.2445 (59)	1 1 2	(O) 3.2445 (54)
	(C) 3.2445		(C) 3.2445
0 4 4	(O) 3.0799 (13)	1 3 1	(C) 3.1646 (12)
	(C) 3.0854		(C) 3.1646
0 7 1	(O) 3.0278 (62)	0 1 6	(O) 3.0386 (57)
	(C) 3.0297		(C) 3.0390
1 3 2	(O) 3.9593 (14)	0 2 5	(O) 3.9695 (15)
	(C) 2 9593		(C) 2.9692
0 2 5	(O) 2.8948 (26)	0 5 5	(O) 2.9311 (36)
	(C) 2.8947		(C) 2.9244
1 4 2	(O) 2.7971 (100)	1 5 1	(O) 2.8063 (100)
	(C) 2.7929		(C) 2.8024
0 6 4	(O) 2.6070 (14)	0 7 7	(O) 2.6221 (18)
	(C) 2.6020		(C) 2.6258
1 8 1	(O) 2.1419 (22)	0 9 4	(O) 2.3212 (12)
	(C) 2.1408		(C) 2.3259
0 2 7	(O) 2.1034 (14)	0 4 3	(O) 2.1467 (18)
	(C) 2.1048		(C) 2.1471
1 9 0	(O) 1.9976 (22)	1 2 4	(O) 2.0717 (21)
	(C) 1.9999		(C) 2.0701
0 6 7	(O) 1.8451 (22)	1 12 1	(O) 1.9976 (33)
	(C) 1.8444		(C) 1.9991
0 12 2	(O) 1.7524 (25)	0 8 7	(O) 1.9812 (30)
	(C) 1.7545		(C) 1.9805
0 9 9	(O) 1.6696 (26)	1 0 9	(O) 1.7648 (24)
	(C) 1.6689		(C) 1.7645
1 3 8	(O) 1.6208 (33)	0 1 11	(O) 1.6668 (21)
	(C) 1.6219		(C) 1.6669
2 4 3	(O) 1.6158 (33)	1 6 9	(O) 1.6158 (27)
	(C) 1.6157		(C) 1.6158

Figure 2 (a-b) shows the variation of dielectric constant (ε) with temperature at four different frequencies (1 kHz, 10 kHz, 100 kHz and 1 MHz) for both the compounds A

and B. Dielectric constant at room temperature increases with decreasing frequency. The higher value of dielectric frequency) indicate that the phase transition is of diffuse type. A particular point cannot be regarded as a definite

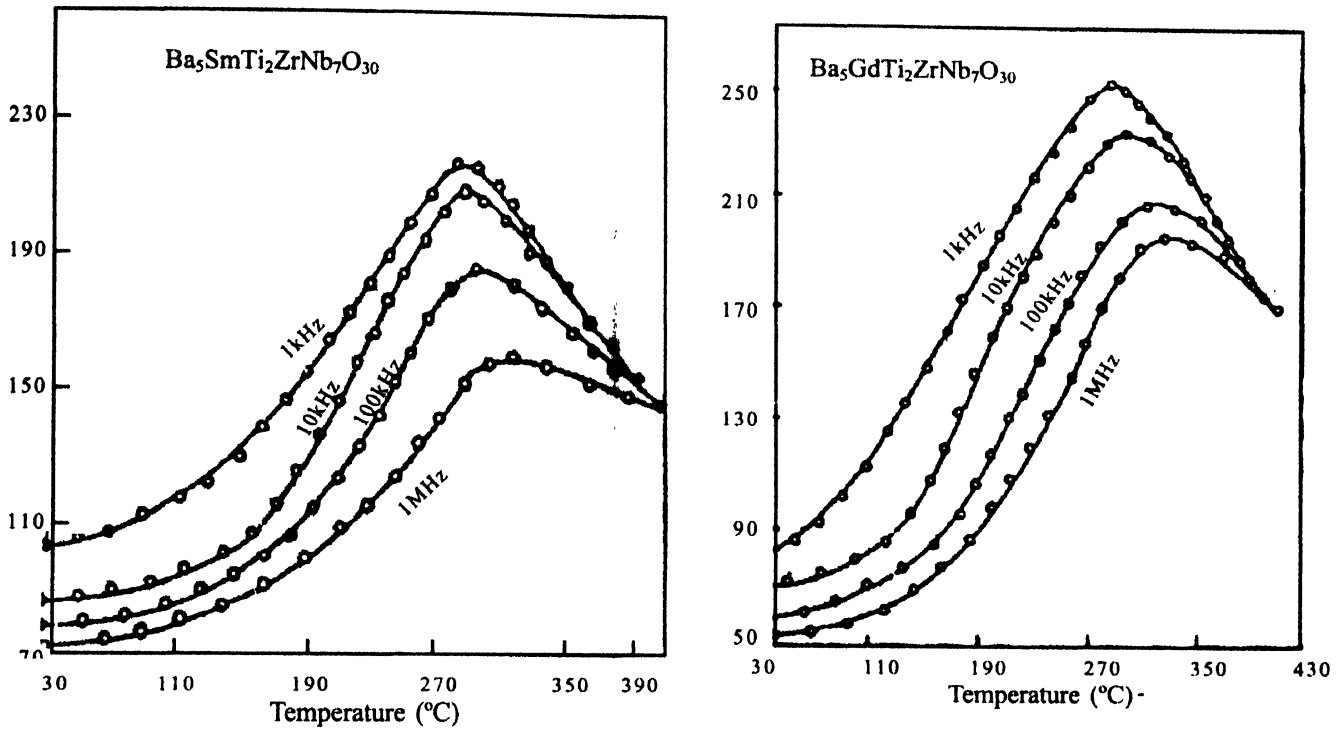

Figure 2. (a-b) Variation of dielectric constant (ε) with temperature of A and B compounds at frequencies 1 kHz, 10 kHz, 100 kHz and 1 MHz.

constant at low frequency is due to the presence of all different types of polarization (electronic, ionic, dipole and space charge) at low frequency. Towards high temperature (beyond transition temperature) ε values for all the four frequency coincide. This shows that these compounds have relaxor behaviour. Dielectric anomaly and phase transition is observed in both the compounds at all the four frequencies. The transition temperature (T_c) is found to shift towards higher temperature side at higher frequencies. This is also the characteristic of relaxor ferroelectric [10]. The values of T_c and maximum dielectric constant (ε_{max}) have been shown in Table 2. The broad dielectric peaks in both the compounds (more at higher Curie point; rather a region called the Curie region is to be

Table 2. Comparison of dielectric properties of A and B compounds at different frequencies.

	Frequency kHz	T_c(°C)	ε_{RT}	ε_{max}	Diffusivity γ
Sm	1	274	102	213	
	10	278	88	208	1.69
	100	286	77	187	
	1000	294	72	159	
Gd	1	278	78	256	
	10	282	63	224	1.60
	100	303	54	206	
	1000	312	48	189	

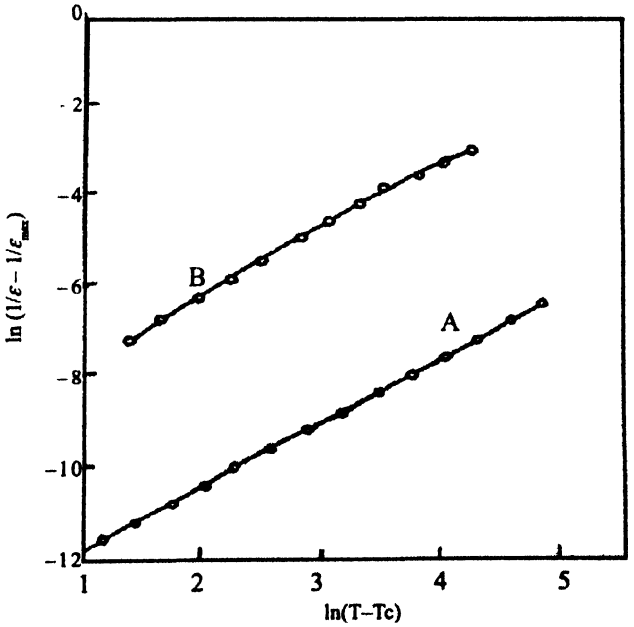

Figure 3. Variation of ln ($1/\varepsilon - 1/\varepsilon_{max}$) with ln ($T-T_c$) of A and B compounds at 10 kHz.

considered. The broadening of the dielectric peaks may be attributed to the different types of disorder and defects in the system. The degree of disordered or the diffusivity (γ) in the system has been calculated using the expression.

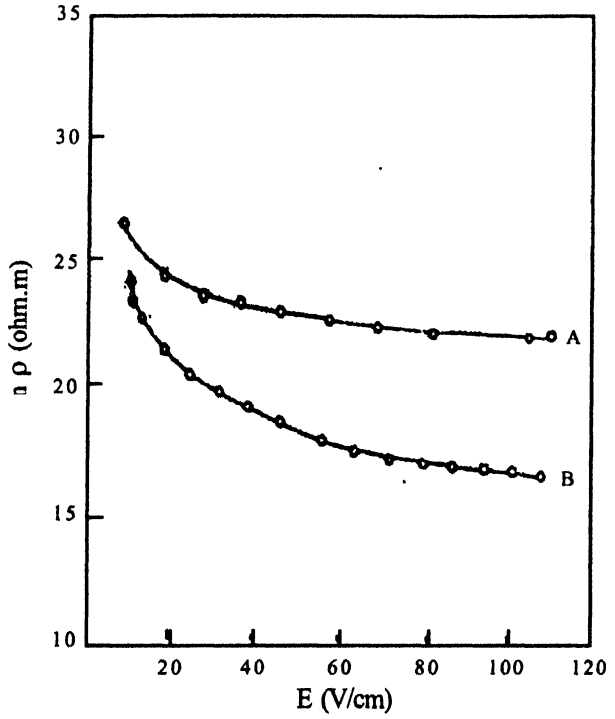

Figure 4. Variation of dc resistivity (ln ρ) of A and B compounds as a function of applied electric field at RT.

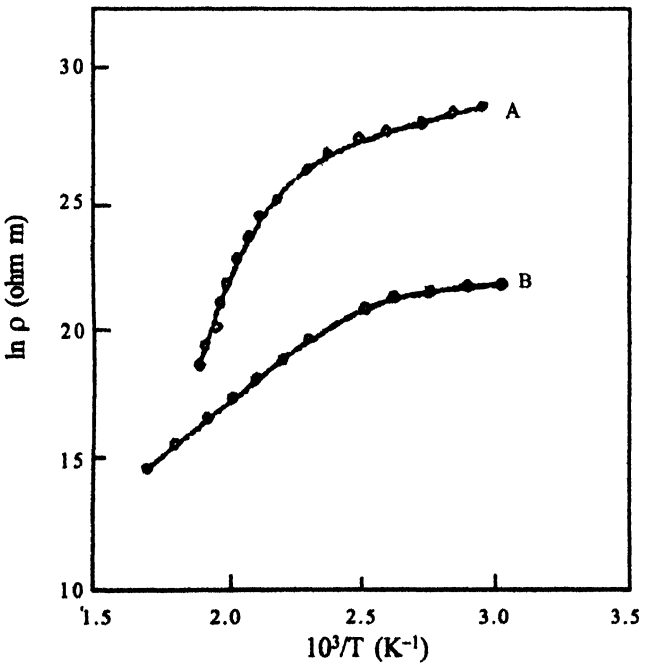

Figure 5. Variation of dc resistivity (ln ρ) with temperature of A and B compounds.

$\ln(1/\varepsilon - 1/\varepsilon_{max}) = \gamma/ \ln (T-T_c)$ + constant [11], where ε_{max} is the maximum value of dielectric constant at T_c.

Figure 3 shows the variation of ln $(1/\varepsilon-1/\varepsilon_{max})$ with ln $(T - T_c)$ for both the compounds A and B at 10 kHz which provides the value of γ (Table 2). The intermediate values of γ between normal ferroelectrics (γ = 1) and highly diffuse type (γ = 2) ferroelectric shows some deviations of transition from Curie-Weiss law. This is an indication of the occurrence of disordering in the system [12].

Figure 4 shows the variation of ln ρ with applied dc voltage of both the compounds A and B at room temperature. The decrease in ln ρ by increasing field is due to alignment of dipoles with the field, which has been observed in many ferroelectrics [13–15].

Figure 5 shows the variation of dc resistivity (ln ρ) with temperature of both the compounds A and B at constant field 100 V/cm. It has been observed that the value of ρ decreases sharply with temperature in the higher temperature region and remains almost constant below100°C. This shows that these compounds have negative temperature coefficient of resistance at higher temperature (above 100°C).

4. Conclusions

Thus it can be concluded that the compounds $Ba_5SmTi_2ZrNb_7O_{30}$ and $Ba_5GdTi_2Nb_7O_{30}$ have orthorhombic structure at room temperature. Both the compounds have diffuse type of ferroelectric phase transition. They show relaxor property and have negative temperature coefficient of resistance at high temperature (above 100°C).

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